INFLUENCE OF CERTAIN PHYSICO-CHEMICAL FACTORS ON THE ADSORPTION CAPACITY OF ACTIVE CARBONS WITH RESPECT TO RHENIUM
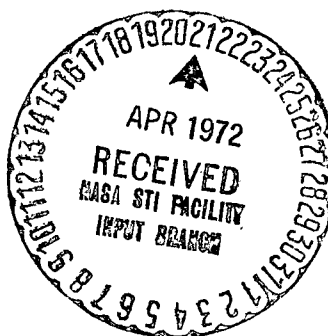
K. B. Lebedev and T. Sh. Tyurekhodzhayeva

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Metallurgii i Obogashcheniye,
Akademii Nauk Kazakhskoy SSR, Vol. 8, 1963,
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INFLUENCE OF CERTAIN PHYSICO-CHEMICAL FACTORS ON THE ADSORPTION CAPACITY OF ACTIVE CARBONS WITH RESPECT TO RHENIUM

K. B. Lebedev and T. Sh. Tyurekhodzhayeva

ABSTRACT. The rhenium adsorption capacity of AG-3 and AG-N carbons is investigated. It is found that the room temperature is the optimum. The admixtures listed in order of increasing harmful influence on adsorption of rhenium are sulfates, chlorides, carbonates, oysulfides, and xanthates.

It has been established previously[1] that the most complete adsorption   /84[*] of rhenium from lean solutions by active carbons is observed at a pH of about 2, and also that AG-3 and AG-N carbons have the greatest adsorption capacity out of all the active carbons produced by domestic industries.

This report studies certain physico-chemical factors influencing the rhenium adsorption capacity of the carbons given above.

Influence of active carbon size. For these studies, a solution containing 30 mg/1 rhenium and a pH equal to 2 was prepared. Three grams of AG-3 carbon were placed in adsorption columns in each experiment. The solution was passed through the columns from bottom to top at a rate of 100 ml per hour at room temperature. The carbon was crushed and divided by sizes of +2; 1; 0.5; 0.25 and — 0.25 mm.

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[1]   Lebedev, K. B., Tyurekhodzhayeva, T. Sh. Vybor adsorbenta i sredy rastvora dlya izvlecheniya reniya i talliya iz bednykh rastvorov (Selection of an Adsorbent and Solution for Extracting Rhenium and Thallium from lean Solutions). Trudy Instituta Metallurgii i obogashcheniya AN KazSSR, Vol. VI, 1963.

[*] Numbers in the margin indicate the pagination in the original foreign text.

As the solution was passed through the adsorption column, 100 ml of filtrate samples were taken, analyzed for rhenium, and the elution adsorption curves were compiled from the analysis data. The results obtained made it possible to determine the dynamic exchange capacity of carbon (DEC) in weight percent, and to calculate the amount of adsorbed rhenium (in mg) and the complete exchange capacity of carbon (CEC) also in weight percent.

The elution curves (1, 2, 3, 4, 5) of this series of experiments are shown in Figure 1, and the basic results are listed in Table 1.

As may be seen from the data obtained, the maximum DEC is observed for a carbon size of — 1 + 0.5 mm, and greatly decreases when larger or smaller sizes are used. The lower value of the DEC or the rapid, so-called "breakthrough" of rhenium in the case of large carbon may be explained by the lower active surface of the large carbon, and also by the fact that ReO_4^- anions cannot penetrate very rapidly into the micropores located within the large carbon particles. The rapid breakthrough in fine carbon may be explained by the fact that a large portion of the rhenium is adsorbed at first not in the carbon pores, but on its surface. After a particular absorption stage, /85 the adsorbed anions are removed by the solution flow.

The maximum CEC value of 6.8-6.9% is observed when larger sizes are used, from — 2 to + 0.25 mm, since during the experiment (which lasts more than 100 hours) there is a regrouping of adsorbed anions and they penetrate into the finest carbon micropores.

Influence of solution filtration rate. Carbon — 0.5 + 0.25 mm in size was used in this series of experiments, and the solution filtration rate was 25, 100, 300 and 500 ml/hr. The other experiment conditions were the same as before. The results obtained are given in Figure 2 and Table 2.

The adsorption rate was always greater than the ion diffusion rate. Therefore, when the solution was passed slowly (25 ml/hr) and when the
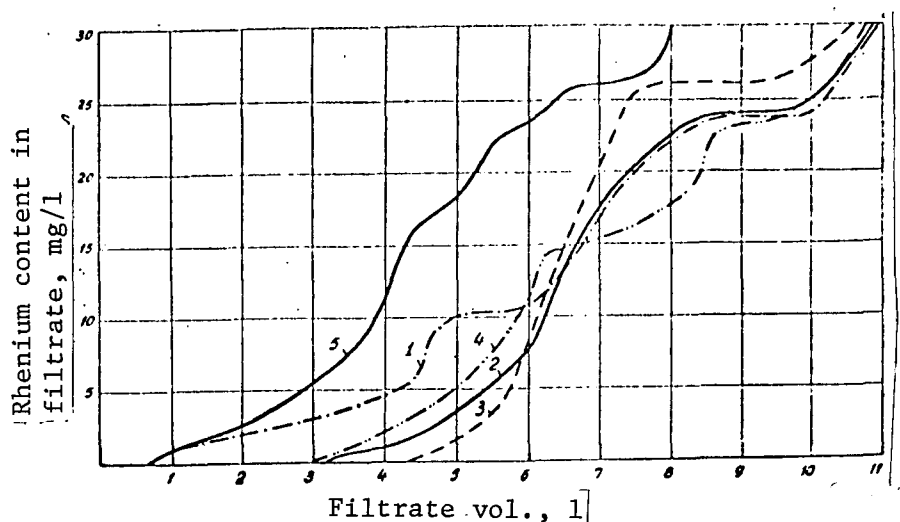
Figure 1. Elution curves for absorption of rhenium
by active carbon of different sizes.

TABLE 1. INFLUENCE OF ACTIVE CARBON SIZE

Expt. No.	Carbon size, mm	DEC, wt., %	Expt. length, hrs	Amt. of absorbed rhenium	CEC, wt. %	$\dfrac{DEC}{CEC}$ 100%
1	+2	0.7	109	197	6.6	11
2	-2 + 1	3.1	109	208	6.9	45
3	-1 + 0.5	4.2	106	204	6.8	62
4	-0.5 + 0.25	3.0	108	208	6.9	44
5	-0.25	0.7	80	135	4.5	16

experiment lasted 264 hours, the ReO_4 anions diffused into the carbon micropores and the DEC increased to 6%, which was 95% of the CEC. For a filtration rate of 100, 300 and 500 ml/hr the DEC was only 3%.

The maximum CEC was observed with a filtration rate of 100 ml/hr. It decreased with a more rapid filtration rate, since the adsorbed anions could not regroup and penetrate into the carbon micropores.

With slow filtration the reduced CEC (Experiment 6, Table 2) may be explained by the fact that during such a long experiment (264 hours) there
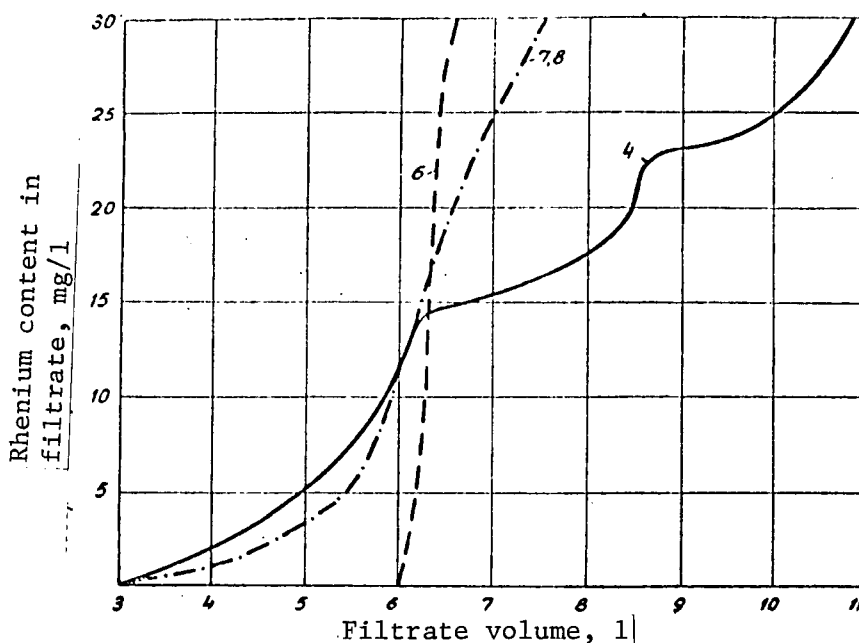
Figure 2. Elution curves for rhenium absorption
by active carbon with different solution
filtration rates.

TABLE 2. INFLUENCE OF SOLUTION FILTRATION RATE

Expt. no.	Solution filtration rate, ml/hr	DEC, wt., %	Expt. length, hrs	Amt. of absorbed rhenium, mg	CEC, wt. %	$\frac{DEC}{CEC}$ 100%
6	25	6.0	264	188	6.3	95
4	100	3.0	108	208	6.9	44
7	300	3.0	25	184	6.1	49
8	500	3.0	15	184	6.1	49

is a more stable accumulation of adsorbed water molecules (as is known, water
is adsorbed by active carbon), and the free activity of the carbon surface
decreases. Another cause may be mechanical disturbance (grinding) of the
microporous structure of the adsorbent.

Influence of rhenium content in initial solution. In this series of experiments, the filtration rate was 100 ml/hr. The other conditions did not change. Solutions containing 5, 30, 100 and 1000 mg/l rhenium were prepared. The results obtained are given in Figure 3 and Table 3, from which it may be seen that, when the rhenium content in the initial solution increases, the DEC increases from 2.2 to 5.7%, and the CEC — from 4.8 to 8.6%. Figure 4 shows the dependence of the DEC and CEC on the rhenium

TABLE 3. INFLUENCE OF RHENIUM CONTENT IN INITIAL SOLUTION

Expt. No.	Conc. in initial solution, mg/l	DEC, wt., %	Expt. length, hrs	Amt. of absorbed rhenium, mg	CEC, wt. %	$\frac{DEC}{CEC}$ 100%
9	5	2.2	378	143	4.8	46
4	30	3.0	108	208	6.9	44
10	100	5.3	36	252	8.4	63
11	1000	5.7	4.5	259	8.6	66

concentration in the initial solution. This dependence may be explained by the fact that, when the ReO_4 anions increase in the solution, there is a greater probability of a large number of these ions penetrating into the micropores. Therefore, the micro- and macropores are filled more densely. /87 The adsorption rate sharply increases. The experiment duration decreases from 378 hours for a rhenium concentration of 5 mg/l to 4.5 hours for 1 g/l.

The maximum CEC value in our experiments was 8.6% for AG-3 carbon. As may be seen from Figure 4, a further increase in the rhenium content in the initial solution will increase the complete exchange capacity of carbon insignificantly up to a certain limit.

Influence of temperature. This series of experiments was performed just as previously, with solutions containing 30 mg/l rhenium. All of the experiments were only performed in the daytime. In this series, experiments No. 12, 13 and 14 (Table 4) were carried out continuously, around the clock,
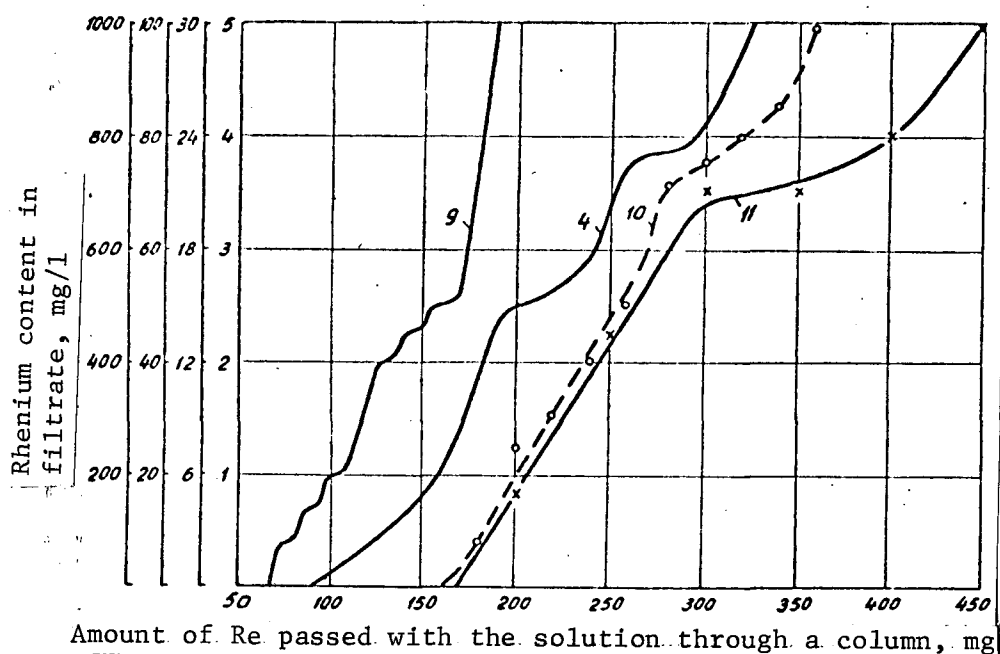
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Figure 3. Elution curves for rhenium absorption
by active carbon from solutions with differing
rhenium content.

at temperatures of 5, 18 and 35°. Columns No. 12 and No. 14 (Figure 5) were placed in a thermostat.

The results obtained are given in Figure 5 and Table 4, where — for purposes of comparison — experiment No. 4 (t = 18°), which is similar to experiment No. 13 is shown, but the column was stopped during the night.

As may be seen from the data obtained, when the temperature increases the DEC increases from 4.3 to 5.3 and 5.5%. This may be explained by the fact that ion diffusion, which limits the total of adsorption process increases, and at the first moment the ReO_4^- anions penetrate deeply into the carbon pores. However, the CEC decreases considerably with a temperature increase, comprising 7.5; 6.9 and 6.4%, respectively, since the rate of the inverse process (desorption) increases. The DEC:CEC ratio sharply changes from 57 (5°) to 77 (18°) and 86 (35°).   /88
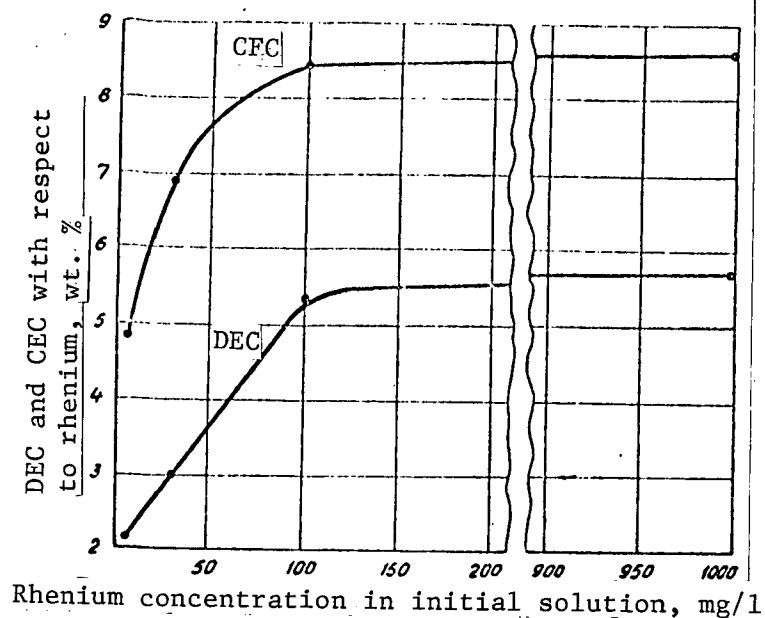
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Figure 4. Dependence of DEC and CEC
on rhenium concentration in initial
solution.

Comparing experiments No. 13 and No. 4 (continuous operation and operation halted during the night), we may reach the conclusion that in the case of continuous operation (when the carbon is in contact with the water containing small amounts of salts for a much longer period of time) active adsorption of water molecules is initially observed. The active carbon surface decreases, and the DEC is 3.0% instead of 5.3% during continuous column operation. However, subsequently there is regrouping of the molecules and ions, and the ReO_4^- anions displaced the adsorbed water molecules, and the CEC in the last analysis has one value, equal to 6.9%, in both cases.

TABLE 4. INFLUENCE OF TEMPERATURE

Expt. No.	Temp. °C	Column operation	DEC, wt., %	Expt. length, hrs	Amt. of absorbed rhenium, mg	CEC, wt. %	$\frac{DEC}{CEC}$ 100%
12	5	continuous	4.3	100	225	7.5	57
13	18	"	5.3	86	207	6.9	77
4	18	stopped at night	3.0	108	208	6.9	44
14	35	continuous	5.5	72	191	6.4	86

Influence of preliminary carbon processing and direction in which solution is supplied. This series of experiments was carried out with AG-N carbon, whose properties in terms of rhenium are identical to those of
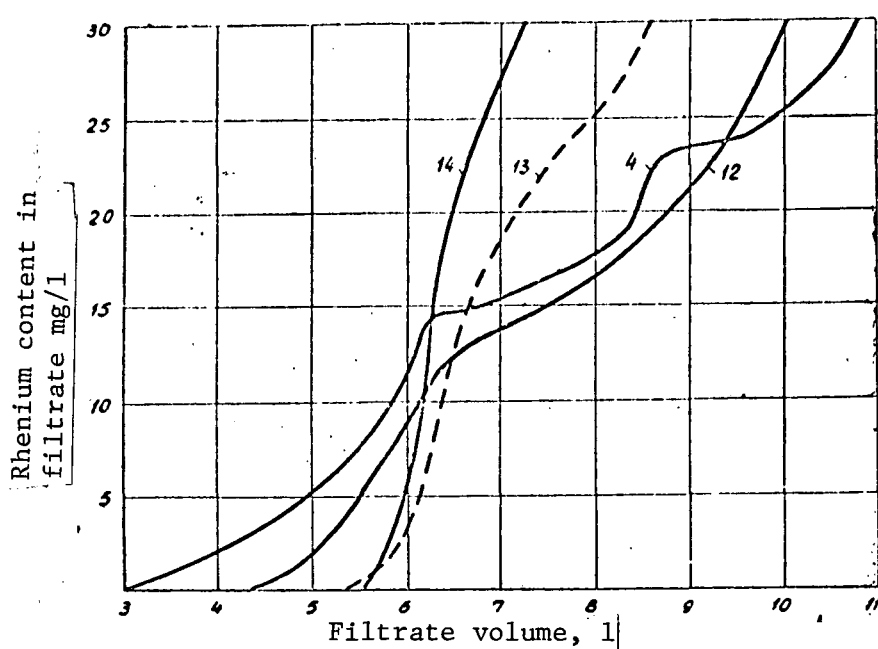
Figure 5.   Elution curves for rhenium absorption
            by active carbon from solutions at differing
            temperatures.

AG-3 carbon. The solution was passed through at a rate of 200 ml/hr. In all   /89

the preceding experiments, after being loaded into the adsorption columns,

the carbon was moistened overnight with distilled water, and was then washed

with a centinormal solution of sulfuric acid until an acidic reaction was

obtained. In this series of experiments, the carbon was used either without

any preparation, or water vapor was passed through the carbon layer for one

hour. In experiments No. 17 and 18 (Table 5), the carbon was prepared as

usual by washing with sulfuric acid, but the solution was supplied both

from below (Experiment No. 17) or from above (Experiment No. 18).

The results obtained are given in Table 5, and the elution curves are

shown in Figure 6.

As may be seen from the data obtained, the earliest breakthrough was

observed when carbon processed with water vapor was used. This may be   /90

explained, in all probability, by a certain disturbance of the active

surface centers of adsorption. The internal carbon structure is not disturbed,

the foreign adsorbed particles are removed, and therefore the CEC is very high
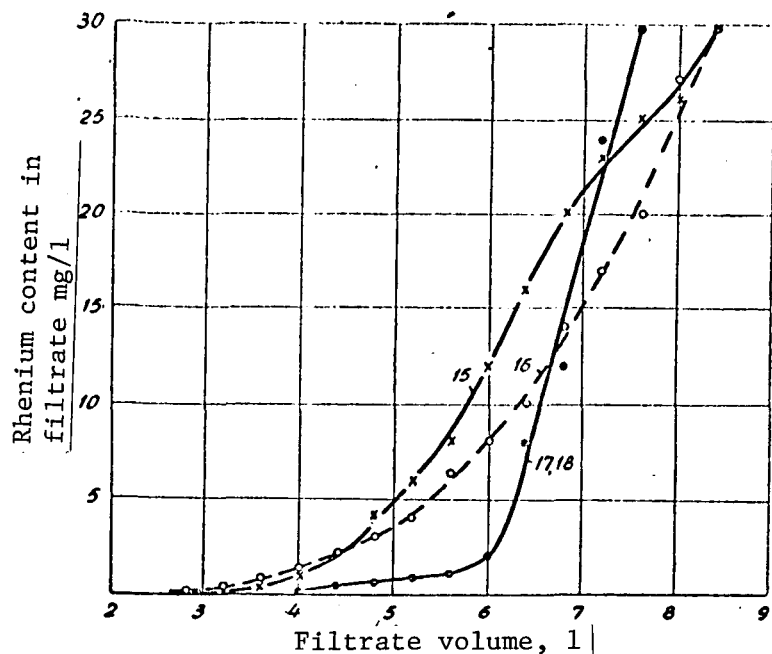
Figure 6. Elution curves for rhenium absorption by active carbon without preliminary carbon processing (Experiment 15), with vapor processing (Experiment 16), and with washing by sulfuric acid (Experiment 17, 18).

— 6.7%. The carbon which has no preliminary processing is used, the DEC increases somewhat, but then the CEC decreases to 6.3%, since molecules and ions may be adsorbed since carbon was stored in its pores previously. Processing with sulfuric acid purifies the surface and pores of carbon from foreign inclusions, and therefore the DEC and CEC are the highest in this case.

As experiments No. 17 and 18 have shown, the solution direction of motion has practically no effect on the dynamic or complete exchange capacity of carbon. This indicates that,

TABLE 5. INFLUENCE OF PRELIMINARY CARBON PROCESSING AND DIRECTION SOLUTION IS SUPPLIED

Expt. No.	Direction solution supplied	Carbon processing before column operation	DEC, wt.,%	Expt. length, hrs	Amt. of absorbed rhenium,mg	CEC, wt.%	$\frac{DEC}{CEC}$ 100%
15	from below	none	3.0	42	188	6.3	48
16	from below	with water vapor	2.6	42	201	6.7	39
17	from below	with 0.01 N sulfuric acid solution	3.8	38	203	6.7	56
18	from above	with 0.01 N sulfuric acid solution	3.8	38	202	6.73	56

for the given experiment method, the carbon does not have a tendency to cake, and no free channels for the passage of the solution are formed.
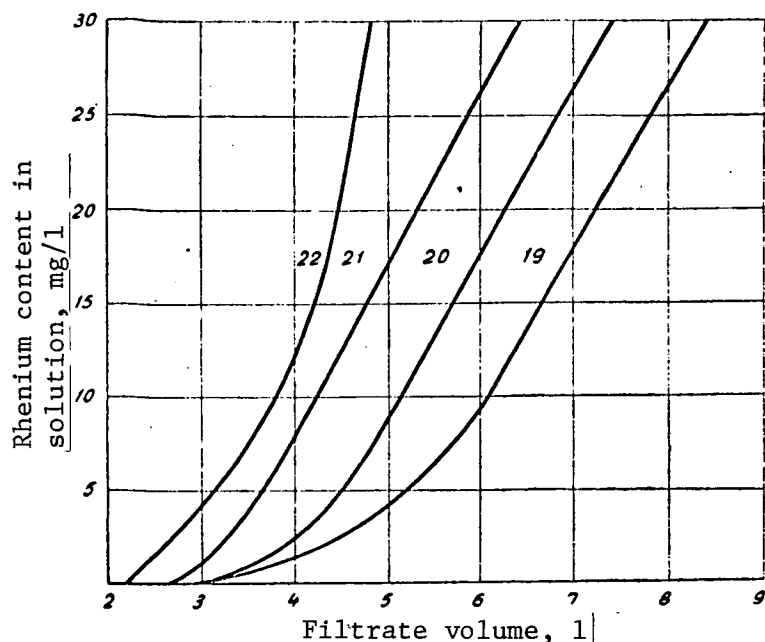
Figure 7. Elution curves for rhenium absorption in one batch of carbon.

Explanation of possible carbon regeneration. In this series of experiments, carbon AG-N was also used.

For the practical application of active carbons, the repeated use of these carbons as rhenium absorbers is very important. In this series of experiments, carbon was saturated with rhenium in the usual manner: 3 g of carbon — 0.5 + 0.25 mm in size were processed with 0.01 N sulfuric acid. The solution containing 30 mg/l of rhenium and having a pH of about 2 was passed through at a rate of 200 ml/hr, and the experiments were carried out at room temperature.

TABLE 6. RESULTS OF FOUR-FOLD ADSORPTION OF RHENIUM IN ONE BATCH OF CARBON (IN THE ADSORPTION-ELUTION CYCLE) |*|

Expt. No.	Order of column saturation	DEC, wt, %	Expt. length, hrs	Amt. of absorbed rhenium, mg	CEC, wt. %	$\frac{DEC}{CEC}$ 100%	Relative DEC decrease, %
19	First	2.8	42	195	6.5	43	100
20	Second	2.8	37	164	5.5	51	85
21	Third	2.6	32	140	4.7	55	72
22	Fourth	2.1	24	116	3.9	54	60

After the complete saturation of the column — i.e., when the rhenium content was 30 mg/l in the filtrate — the experiment was ended. Washing out the rhenium from the column — elution — was performed with 30 g/l of soda solution at a temperature of 80°, and the solution was passed through at a rate of 60 ml/hr. 10 ml of samples were collected every 10 minutes. The /91

*Translator's Note: The foreign text is inconsistent in the use of adsorb and absorb in Tables 6, 7 and 8.
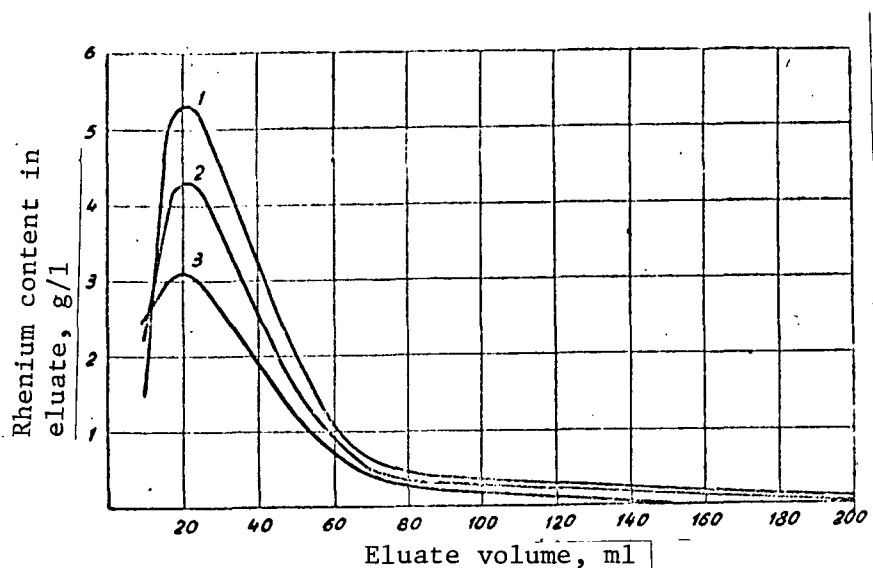
Figure 8. Elution curves. The numbers
designate the elution number.

total eluate volume was about 300 ml. Elution was more than 95% complete
in every case.

After elution, the column was washed with 0.01 N sulfuric acid until
an acidic reaction was obtained, and the second saturation of the column was
performed. Four-fold saturation of the column was performed according to
this cycle with three-fold elution. There was no point in performing a
fourth elution, which is clear from the following considerations. The
saturation results obtained are given in Figure 7 and Table 6, and the elution
curves are given in Figure 8.

As may be seen from the data obtained, with repeated saturation of
carbon the DEC decreases very little, from 2.8 to 2.1%. However, the CEC
decreases considerably from 6.5 to 3.9%. With the fourth saturation of the
column, the complete exchange capacity of carbon is 60% of the initial
capacity.

A reduction in the carbon activity as a result of repeated regeneration
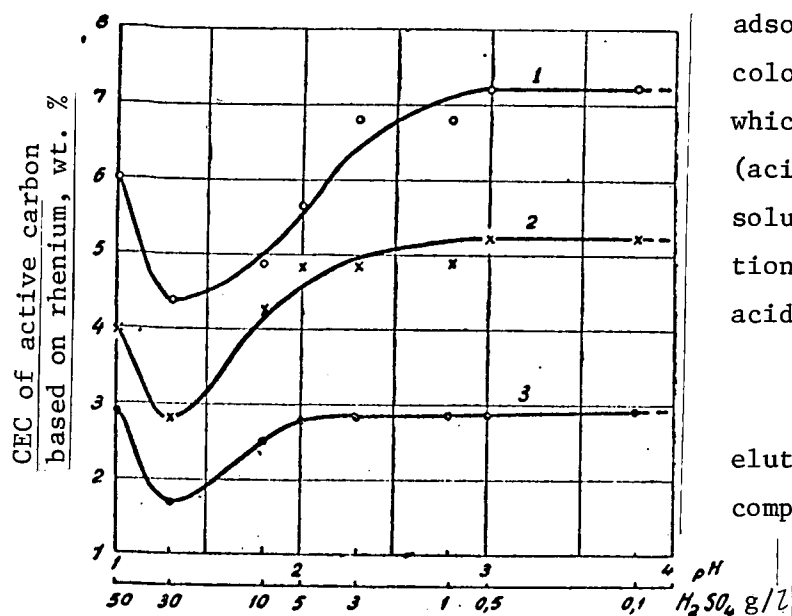may be explained both by a certain mechanical disturbance of the active

Figure 9. Influence of solution acidity and adsorbent excess on CEC of active carbon with respect to rhenium. Carbon batch, mg: 1 — 5; 2 — 10; 3 — 20.

adsorption centers, and by colonization of the micropores which is produced by sodium-sulfate /92 (acidification of the initial solutions to pH = 2   and preparation of the carbon by sulfuric acid).

As may be seen from Figure 8, elution occurs very actively and completely.

This series of experiments has shown the possibilities of performing 3 - 4-fold use of carbon in industry after elution of rhenium by hot soda solutions.   /93

Determining the static exchange capacity (SEC) of active AG-3 carbon. The purpose of this series of experiments was to determine the SEC of active carbon as a function of the solution acidity and the adsorbent excess. The procedure used in the experiments was based on the fact that, under certain industrial conditions, it is advantageous to perform adsorption periodically in agitation tanks, and not in adsorption columns.

The experiments were carried out as follows. 5.10 or 20 mg of carbon, with a size of —0.5 + 0.25 mm, were placed in a test tube with a capacity of 50 ml. Twenty ml of a solution containing 30 mg/l rhenium and from 0.1 to 50 g/l sulfuric acid were added. The rhenium content was 35 mg/l in experiments using a 5 mg sample. The test tubes were closed with a rubber stopper attached to a disk rotating at a rate of 60 rpm, and they were rotated for 6 hours at room temperature. After the experiment had ended, the residue was filtered, and the rhenium content in the solution was determined.

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TABLE 7.   STATIC EXCHANGE CAPACITY (CSEC) OR AG-3 CARBON WITH RESPECT
          TO RHENIUM AS A FUNCTION OF THE SOLUTION ACIDITY AND ADSORBENT
          EXCESS.

(Decimal points appear as commas)

| Expt. No. | H_2SO_4 conc. in. sol. g/l | Approx. pH | 5 mg carbon | | | |
			Rhenium content in filtrate, mg/1	Rhenium absorbed, rel. %	Rhenium absorbed, mg	CEC wt., %
1	0,1	3 8	17,0	51,5	0,36	7,2
2	0,5	3,0	17,0	51 5	0.36	7.2
3	1	2,8	18 0	48 6	0 34	6 8
4	3	2,3	18.0	48.6	0,34	6,8
5	5	2,0	21,0	40.0	0,28	5,6
6	10	1,8	23 0	34.4	0.24	4 8
7	30	1,3	24 0	31.5	0,22	4,4
8	50	1,0	20,0	42,8	0,30	6,0

| Expt. No. | H_2SO_4 conc. in. sol. g/l | Approx. pH | 10 mg carbon | | | |
			Rhenium content in filtrate, mg/1	Rhenium absorbed, rel. %	Rhenium absorbed, mg	CEC wt., %
1	0,1	3 8	4,0	86 6	0.52	5,2
2	0,5	3,0	4,0	86,6	0,52	5,2
3	1	2,8	5.5	81,0	0,49	4,9
4	3	2,3	6,0	80,0	0,48	4,8
5	5	2,0	6,0	80.0	0,48	4,8
6	10	1,8	9,0	70,0	0.42	4,2
7	30	1,3	16 0	46,5	0.28	2,8
8	50	1,0	10,0	66,6	0,40	4,0

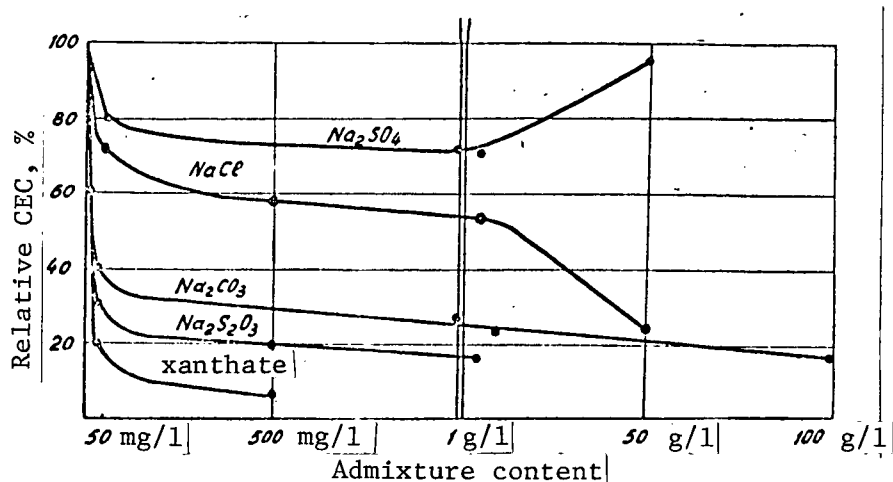| Expt. No. | H_2SO_4 conc. in. sol. g/l | Approx. pH | 20 mg carbon | | | |
			Rhenium content in filtrate, mg/1	Rhenium absorbed, rel. %	Rhenium absorbed, mg	CEC wt., %
1	0,1	3 8	1,0	96.7	0 58	2 9
2	0,5	3,0	1,0	96.7	0,58	2,9
3	1	2,8	1,5	95.0	0.57	2,85
4	3	2,3	2,0	93.3	0,56	2,8
5	5	2,0	2.4	92,0	0,55	2,75
6	10	1,8	5,0	83.4	0,50	2,5
7	30	1,3	13,5	55.0	0,33	1,7
8	50	1,0	1,0	96,8	0,58	2,9

Figure 10. Influence of admixtures in initial
solution on relative CEC of active carbon with
respect to rhenium.

The results obtained are given in Table 7, and are shown graphically
in Figure 9.

As may be seen from the data obtained, when the pH increases from 1 to
approximately 1.3 (30 g/l H_2SO_4), the SEC decreases considerably, and then
sharply rises at pH = 2, 3, 4. As was known from the previous experiments, a
further increase in the pH leads again to a sharp decrease in the adsorption
capacity of active carbon.

An increase in the SEC with a decrease in the carbon may be explained
by a decrease in its excess with respect to rhenium. A further decrease
in the carbon would lead to great errors in the analysis and the computations.
Therefore, we confined ourselves to determining the static exchange capacity
as a function of specific conditions, and did not determine the complete
static exchange capacity — CSEC.   /94

These experiments have shown that it is not advantageous to extract
rhenium from lean solutions by agitation (mixing) of solutions with active
carbon. This is due to the fact that in one operation it is possible to

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obtain filtrates containing up to 1 mg/l rhenium with a 2.9% saturation
of carbon (see Table 7, No. 1 and 2; carbon — 20 mg). Lowering the
carbon consumption may increase the degree to which it is saturated with
rhenium, due to the increased amount which remains in solution, which
requires the installation of several agitators.

Influence of anions contained in industrial and natural solutions on
the rhenium adsorption capacity of active carbons. In addition to rhenium,
several other salts pass into solution after the reprocessing of rhenium-
containing materials (copper and molybdenum concentrates, roasted with
powder and converter powders). In addition to the ReO_4^- anion, SO_4'', CO_3'',
Cl', S_2O_3'' anions and xanthate-ion are most frequently present in the solutions.

Several experiments with artificially prepared solutions were carried
out to clarify the influence of these anions. These anions were introduced
in a sodium form into a solution of calcium perrenate in distilled water.
There was no acidification or alkalization of the solutions.

The experiments were performed in adsorption columns by the dynamic method
according to the method indicated above. The rhenium content in the initial
solution was 30 mg/l; the admixture content ranged from 5 mg/l to 100 g/l.
Three grams of AG-N carbon were used, in a size of —0.5 + 0.25 mm. The
solution was passed through at a rate of 200 ml/hr; room temperature was
observed.

The results obtained are given in Table 8 and Figure 10, where the
relative decrease in the CEC from the amount of admixtures in the initial
solution is given and and not the elution curves for each experiment. As
may be seen from the data obtained, the most harmful admixture is xanthate,
which is readily adsorbed by carbon and sharply decreases the activity of
the latter with respect to rhenium.

TABLE 8. INFLUENCE OF ADMIXTURE CONTENT IN INITIAL SOLUTION ON ADSORPTION CAPACITY OF ACTIVE CARBON WITH RESPECT TO RHENIUM.

TABLE 8 (Decimal points appear as commas)

Expt. no.	Sodium sulfate	Sodium carbonate	Sodium chloride	Sodium hyposulfite	Sodium xanthate	DEC, wt.,%	Expt. length, hrs	Amt. of absorbed rhenium, mg	CEC, wt.%	DEC/CEC 100%	Relative CEC change, %
1	none	none	none	none	none	2,4	29	123	4,1	59	100
2	0,05					1,2	29	99	3,3	36	80
3	1					1,0	26	89	3,0	33	73
4	5					1,0	23	87	2,9	35	71
5	50					2,2	27	116	3,9	56	95
6	none	0,035				0,6	14	52	1,7	35	41
7		1				0,3	7	32	1,1	27	27
8		10				0,0	8 5	30	1,0	—	24
9		100				0,0	6	20	0,7	—	17
10		none	0,035			1,0	22	89	3,0	33	73
11			0,5			0,4	20	73	2,4	17	59
12			5			0,8	15	65	2,2	36	54
13			50			0,0	11	31	1,0	—	24
14			none	0,005		1,2	19	79	2,6	46	63
15				0,035		0,4	11	40	1,3	31	32
16				0,5		0,0	9	23	0,8	—	20
17				5,0		0,0	8	21	0,7	—	17
18				none	0,010	0,2	21	74	2,5	8	61
19					0,035	0,1	13	25	0,8	12	20
20					0,5	0,0	3	10	0,3	—	7

The harmful influence of oxysulfides in the solution may be explained by their oxidizing capacity, as a result of which the activity of the carbon adsorption centers is reduced. Sodium carbonate sharply increases the pH of the solution, which makes the adsorption conditions worse.

The presence of 1 g/l sodium chloride reduces the CEC by almost a factor of two, and 50 g/l — almost by 25%.

Sodium sulfate initially lowers the carbon activity with respect to rhenium by 25 - 30%. However, with a content of 50 g/l, its activity is restored. Analyses of the filtrates of the sulfate-ion showed that the latter is not adsorbed by carbon. In all probability, an increase in the sulfate content in the solution contributes to the salting out of rhenium.

CONCLUSIONS

The following optimal conditions for rhenium adsorption from solutions by active carbon have been established:

1. The carbon size is — 1 + 0.5 mm. 2. The solution is passed through at no more than 100 ml/hr for three grams of carbon. The greatest DEC and CEC values are reached when rhenium is extracted from solutions containing more than 100 mg/l of rhenium. 4. To increase the DEC, the solutions must be heated; to increase the CEC — they must be cooled. The optimal temperature for both indices is room temperature. 5. In order to increase the carbon activity with respect to rhenium, the latter must be washed with a weak solution of sulfuric acid (0.01N) before being used. 6. The direction in which the solution is passed through the column does not matter. 7. Rhenium can be extracted from carbon (elution) very well by hot solutions of soda. 8. Carbon can be regenerated 3 - 4 times during elution of rhenium with soda solutions, after which its activity with respect to rhenium decreases to 60% of the initial value. 9. It is not advantageous to carry out adsorption of rhenium from solutions with active carbons by mixing

(agitation), since this complicates the equipment for the process.

The influence of certain anions contained in industrial and natural solutions has been established. The admixtures may be arranged in the following order in terms of increasing harmful influence on adsorption of rhenium: sulfates, chlorides, carbonates, oxysulfides, and xanthates.